

Proposed Amendments to the Test Methods Sections of the Consumer Products Regulation and the Antiperspirant and Deodorant Regulation

[Note: The proposed amendments are shown below in underline to indicate additions and ~~strikeout~~ to show deletions.]

Amend Section 94506 (a), Title 17, California Code of Regulations, to read as follows:

94506. Test Methods

- (a) Testing to determine the volatile organic compound content of an antiperspirant or deodorant, or to determine compliance with the requirements of this article, shall be performed using ~~one or more of the following analytical methods which are incorporated by reference herein: (1) Method 24-24A, Part 60, Title 40, Code of Federal Regulations, Appendix A, July 1, 1988; (2) Method 18, Federal Register 48, no. 202, October 18, 1983; (3) Method 1400, (NIOSH Manual of Analytical Methods, Volume 1, February 1984; or (4) Environmental Protection Agency Method 8240, "GC/MS Method for Volatile Organics," September 1986~~ Air Resources Board Method 310, Determination of Volatile Organic Compounds (VOC) in Consumer Products, adopted [date of adoption], which is incorporated herein by reference. Alternative methods which are shown to accurately determine the concentration of VOCs in a subject product or its emissions may be used upon approval of the Executive Officer.

Amend Section 94515 (a), Title 17, California Code of Regulations, to read as follows:

94515. Test Methods

- (a) Testing to determine compliance with the requirements of this article, shall be performed using ~~one or more of the following analytical methods which are incorporated by reference herein: (1) Method 24-24A, Part 60, Title 40, Code of Federal Regulations, Appendix A, July 1, 1988; (2) Method 18, Federal Register 48, no. 202, October 18, 1983; (3) Method 1400, (NIOSH Manual of Analytical Methods, Volume 1, February 1984; or (4) Environmental Protection Agency Method 8240, "GC/MS Method for Volatile Organics," September 1986~~ Air Resources Board Method 310, Determination of Volatile Organic Compounds (VOC) in Consumer Products, adopted [date of adoption], which is incorporated herein by reference. Alternative methods which are shown to accurately determine the concentration of VOCs in a subject product or its emissions may be used upon approval of the Executive Officer.

PROPOSED

STATE OF CALIFORNIA
CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
AIR RESOURCES BOARD

METHOD 310

**DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN
CONSUMER PRODUCTS**

Adopted:

[date of adoption]

DISCLAIMER: Mention of any trade name or commercial product in Method 310 does not constitute endorsement or recommendation of this product by the Air Resources Board.

DRAFT METHOD 310
DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN
CONSUMER PRODUCTS

1.0 APPLICABILITY

This method applies to the determination of the percent by weight of volatile organic compounds (VOC) in consumer products and antiperspirant and deodorant products, as defined in Title 17, California Code of Regulations, sections 94500 - 94517. This method does not apply to the determination of the composition or concentration of fragrance components in products.

2.0 TEST METHODS

California Air Resources Board (ARB) Method 310 incorporates by reference the following American Society for Testing and Materials (ASTM), National Institute for Occupational Safety and Health (NIOSH), and United States Environmental Protection Agency (U.S. EPA) analytical test methods:

- 2.1 ASTM D2369-87: Standard Test Method for Volatile Content of Coatings (June 10, 1987).
- 2.2 ASTM D1426-93: Standard Test Methods for Ammonia Nitrogen in Water (September 15, 1993).
- 2.3 ASTM D4017-88: Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (October 31, 1988).
- 2.4 ASTM D3792-86: Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph (November 28, 1986).
- 2.5.ATSM D2887-93: Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (determination of hydrocarbon content greater than 12 carbons in alkyl mixtures) with (August 15, 1993).
- 2.6 ASTM D859-88: Standard Test Method for Silica in Water (determination of polymethylsiloxanes after digestion) (August 19, 1988).

- 2.7 ASTM D2879-92: Standard Test Method for Vapor Pressure-Temperature Relationship and Initial Decomposition Temperature of Liquids by Isoteniscope (October 15, 1992).
- 2.8 ASTM E1131-86: Standard Test Method for Compositional Analysis by Thermogravimetry (September 26, 1986).
- 2.9 ASTM D3074-72: (Reapproved 1988) Standard Test Methods for Pressure in Metal Aerosol Containers (Approved July 28, 1972 and reapproved in 1988).
With the modifications found in Appendix A.
- 2.10 ASTM D3063-79: (Reapproved 1984) Standard Test Methods for Pressure in Glass Aerosol Bottles (April 27, 1979 and reapproved in 1984). With the modifications found in Appendix A.
- 2.11 ASTM D3064-89: Standard Terminology Relating to Aerosol Products (November 24, 1989).
- 2.12 NIOSH: Method 1400 Alcohols I (analysis of acetone and ethanol by gas chromatography). NIOSH Manual of Analytical Methods, Volume 1 (February 1984).
- 2.13 U.S. EPA Method 8240, September 1986 revision 0, Gas Chromatography/Mass Spectrometry for Volatile Organics (analysis of exempt and/or prohibited compounds in the product by headspace/gas chromatography/mass spectrometry), Test Methods for Evaluating Solid Waste, Volume 1B: Laboratory Manual Physical Chemical Methods, SW-846, November 1986.
- 2.14 U.S. EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings: Code of Federal Regulations (CFR) Part 60, 40 Appendix A, as it existed on July 1, 1994.
- 2.15 U.S. EPA Reference Method 24A, Determination of Volatile Matter Content and Density of Printing Inks and Related Coatings: 40 CFR Part 60, Appendix A, as it existed on July 1, 1994.

2.16 U.S. EPA Reference Methods 18, Measurement of
Gaseous Organic Compound Emissions by Gas
Chromatography: 40 CFR Part 60, Appendix A, as it
July 1, 1994. existed on

3.0 PROCEDURE

The following tests shall be performed on product samples:¹

- 3.0.1 Gravimetric analysis of samples to determine the weight percent of Total VOC in the non-propellant portion, using ASTM D2369-87.
 - 3.0.2 Determination of sample water content. For determination of water content either ASTM D4017-88 or ASTM D3792-86 may be used.
 - 3.0.3 Determination of ammonium content, using ASTM D1426-93.
 - 3.0.4 Determination of ketones and alcohol content using NIOSH 1400.
 - 3.0.5 For aerosol products only, an analysis of sample propellant should be performed using method U.S. EPA Method 18 and ASTM D3074-72 (as modified) or ASTM D3063-79 (as modified).
 - 3.0.6 Analysis of exempt and prohibited compounds, if present (U.S. EPA Method 8240, ASTM D2887-93, ASTM D859-88, NIOSH 1400).
- 3.1 If the above tests indicate that a product does not comply with the applicable regulatory standards, the sample shall be re-analyzed to confirm the results.
 - 3.2 Data will be reported to the Air Resources Board's Compliance Division or the appropriate laboratory client. Only those components with concentrations equal to or greater than 0.1 percent by weight shall be reported.
 - 3.3 If a sample is found to contain compounds prohibited as ozone depleters at concentrations equal to or exceeding 0.1 percent by weight, the sample will be re-analyzed for confirmation. If confirmed the Compliance Division will be notified.
 - 3.4 Request for Air Resources Board consumer product laboratory data shall be directed to the Chief, Compliance Division or the appropriate laboratory client.

¹ Approved alternative test methods may be used, as provided in 5.0.

4.0 DETERMINATION OF VOC CONTENT

4.1: Aerosol Products

For aerosol products, the percent VOC content shall be calculated using the following equation:

$$\text{PERCENT VOC} = \frac{\text{WL(TV-A-H-EL)} + \text{WP} - \text{EP}}{\text{WL} + \text{WP}} \times 100\%$$

Where²:

WL = weight (gm) of liquid product excluding container and packaging

TV = weight fraction of non-propellant total volatile material (ASTM D2369-87)

A = weight fraction of ammonia (as NH₄) in liquid (ASTM D1426-93)

H = weight fraction of water in liquid (ASTM D3792-86 or ASTM D4017-88)

EL = weight fraction of exempt compounds in liquid (U.S. EPA Method 8240, ASTM D2887-93, ASTM D859-88, NIOSH 1400)

WP = weight (gm) of propellant (ASTM D3074-72 [as modified] or ASTM D3063-79 [as modified])

EP = weight (gm) of exempt compounds in propellant (U.S. EPA Method 18)

4.2: Non-Aerosol Products

For non-aerosol products, the percent VOC content shall be calculated using the following equation:

² Approved alternative test methods may be used, as provided in 5.0.

$$\text{PERCENT VOC} = (\text{TV-A-H-EL}) \times 100\%$$

5.0 ALTERNATE TEST METHODS

Alternative test methods which are shown to accurately determine the concentration of VOCs or constituent components in consumer products and antiperspirant/deodorants or their VOC emissions may be used upon written approval of the Executive Officer of the ARB.

Appendix A

ASTM D3074-72 and D3063-79 MODIFICATIONS

1.0 SUMMARY OF MODIFICATIONS

This procedure modifies ASTM D3074-72 and D3063-79 to allow collection of the propellant for analysis and density measurement. The aerosol product container is pierced and the propellant is bled into an evacuated manifold. After the manifold reaches atmospheric pressure, approximately 1 liter of the propellant is collected in a clean, evacuated tedlar bag. For density measurement the propellant is collected into an evacuated 250 ml glass dilution bulb that has been weighed to the nearest 0.1 mg. After filling, the dilution bulb is re-weighed to determine the density of the propellant. Alternately, density may be determined using a Density/Specific Gravity Meter. The tedlar bag with the propellant aliquot is taken to the laboratory for analysis.

2.0 LIMITATIONS

Nitrogen analysis: Nitrogen may be used as a component of the propellant system. Ambient air is 78 percent nitrogen and may be present as a contaminate in the system prior to sample collection. This is eliminated by completely evacuating the propellant collection system and sweeping out any connecting lines to the tedlar bag with product before starting sample collection. This procedure will eliminate or reduce nitrogen contamination to less than 0.1% by weight of the sample and the analysis of the propellant gas will be unaffected.

3.0 APPARATUS AND MATERIALS

- 3.1 Propellant Collection System³: See Figure 1. The system was built from 1/4" stainless steel and Teflon tubing. The vacuum pump is of bellows diaphragm design.
- 3.2 Tedlar Bags, 1 liter, equipped with slip valve and septum
- 3.3 Density Measurement

³ The metal piercing adapter is available from Mid-West Screw Products, Inc., 3523 North Kenton Ave., Chicago, IL 60641. Interim Part Number: 8013A-3/4 Longer SS. The gasket is available from Alltech Associate 2051 Waukegan road, Deerfield, IL 60015, part number 80-16. The glass aerosol adapter is available from Modern Machine Ship, Inc. P.O. Box 826, 123 N. Hazel Street, Danville, IL 61832.

3.3.1 250 ml gas dilution bulb

3.3.2 or, an Density/Specific gravity meter meeting the following minimum specifications:

3.3.2(a). Measurement Method: Natural Oscillation Type

3.3.2(b). Range: 0 - 3g/cm³

3.3.2(c). Measurement Temperature Range: 4°C ~ 70°C.

3.3.2(d). Temperature Accuracy: +/- 0.02°C (10°C ~ 30°C) and +/-0.05°C (4°C ~70°C).

3.3.2(e). Temperature Control Accuracy: +/- 0.01°C.

3.3.2(f). Measurement Time: 1- 4 minutes.

3.4 Gas tight syringe, 100 FI

3.5 Balance, capable of accurately weighing to 0.1 mg

3.6 Can Piercing Platform. See Figure 2 (metal cans) and Figure 3 (glass containers).

3.7 Platform Shaker, equivalent to Thermolyne M49125

4.0 PROCEDURE

4.1 Propellant Collection for Metal Aerosol Containers

4.1.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).

4.1.2 Remove the valve actuator on the aerosol can and weigh can to the nearest 0.01 g. Invert the can into cork holding ring on the piercing apparatus, center and snug against the gasket. (Figure 2)

4.1.3 Connect tedlar bag to output 2, evacuate bag and seal. Connect 250 ml glass dilution bulb to output 1, evacuate bulb and seal.

- 4.1.4 Slowly raise the hydraulic jack until the can is pierced. Record the pressure of the can.
- 4.1.5 Vent the can until the pressure is at about 25 psi. Collect the propellant in the tedlar bag.
- 4.1.6 After the propellant is collected, close and remove the tedlar bag and vent the remainder of the propellant.
- 4.1.7 Weigh the evacuated 250 ml bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.
- 4.1.8 After the flow ceases from the can, it is removed from the assembly and allowed to vent overnight. The can may be placed on a platform shaker to vent the remainder of the propellant.
- 4.1.9 Reweigh can to the nearest 0.01 gm and record weight loss (total gms propellant). The can may now be opened for analysis of the liquid product.
- 4.2 Propellant Collection for Glass Aerosol Containers
 - 4.2.1 Turn on vacuum pump, close valves and evacuate the system (see Figure 1).
 - 4.2.2 Connect tedlar bag to output 2, evacuate bag and seal. Connect 250 ml glass dilution bulb to output 1, evacuate bulb and seal
 - 4.2.3 The gauge assembly is prepressurized in order to minimize product expulsion and system contamination.
 - 4.2.4 Remove actuator from valve of the aerosol glass container, and weigh container to the nearest 0.01gm.
 - 4.2.5 With container in an inverted position place the valve onto the tapered adaptor. Bring the top plate down to the flat of the container and tighten the nuts. A cork ring may be required to stabilize the container.

- 4.2.6 Record pressure of container and vent until the pressure is approximately one-half of recorded pressure. Collect propellant sample into the tedlar bag.
- 4.2.7 After the propellant is collected, close and remove the tedlar bag and vent the remainder of the propellant.
- 4.2.8 Weigh the evacuated 250 ml bulb to the nearest 0.1 mg. Use gloves while handling the bulb. Connect the bulb to the tedlar bag and open to fill the bulb. Close the valves and re-weigh the dilution bulb, record the weight gain and calculate the propellant density in gm/l.
- 4.2.9 Continue to vent container on the platform assembly overnight.
- 4.2.10 Remove container from platform and loosen valve assembly, do not remove valve assembly at this time.
- 4.2.11 Placed container on a platform shaker to vent the remainder of the propellant.
- 4.2.12 Reweigh container and valve assembly to the nearest 0.01 gm and record weight loss (total gms propellant). The container may now be opened for analysis of the liquid product.

FIGURE 1

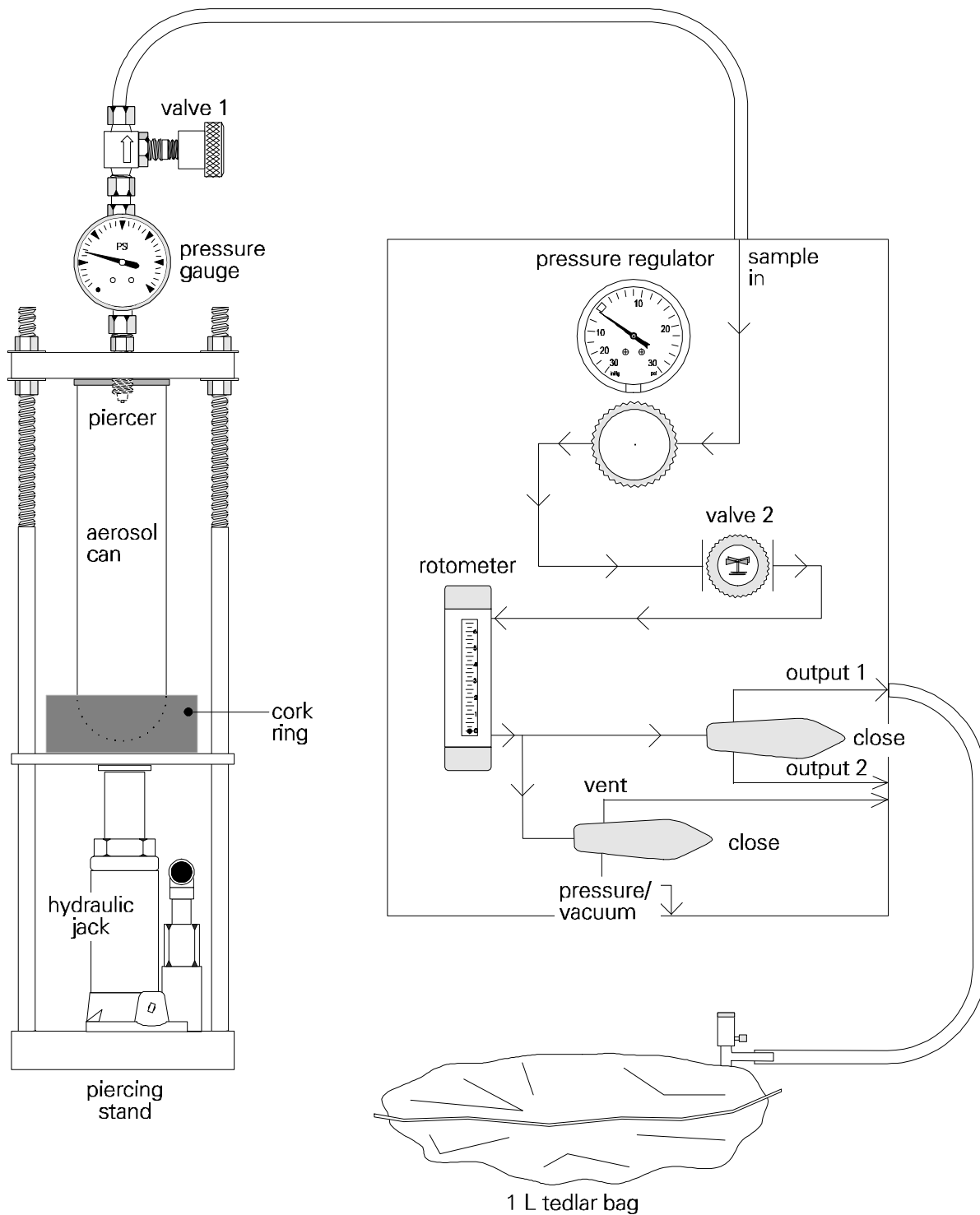


FIGURE 2

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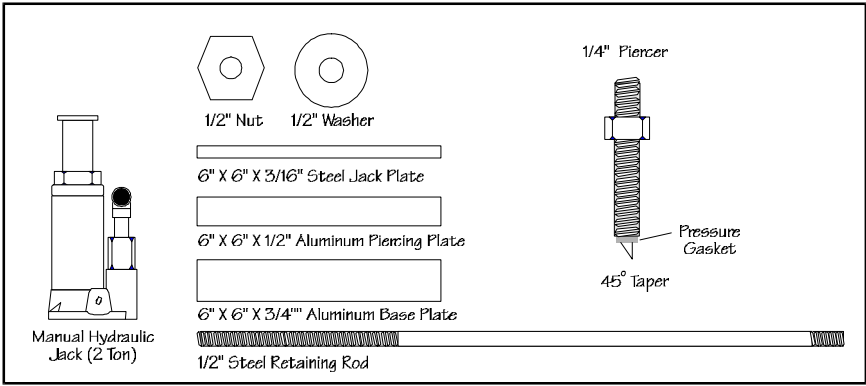
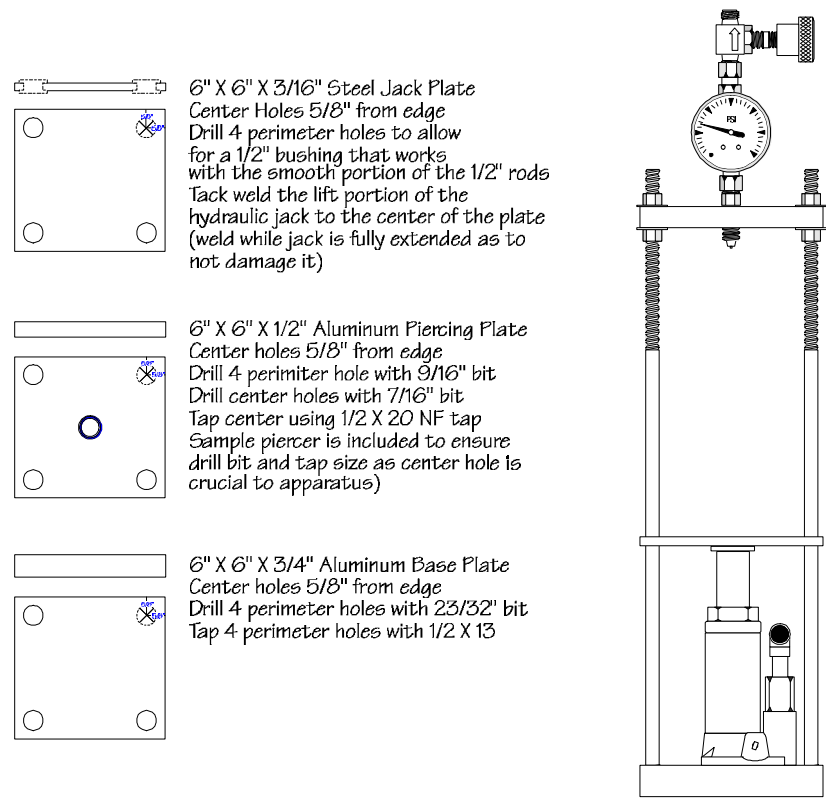


FIGURE 3

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